

OH defects in hydrothermally synthesized monazite (LaPO₄) and xenotime (YPO₄) single crystals

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Monazite and xenotime are common REE (rare earth elements: here considered as Y and lanthanoid) minerals in crustal metamorphic and granitic rocks (e.g. Spear and Pyle 2002). These minerals are widely used in petrologic studies as a U-Th-Pb geochronometer (e.g. Parrish 1990, Suzuki et al. 1991) and a geothermometer (e.g. Gratz and Heinrich 1997, Pyle et al. 2001 and Viskupic and Hodges 2001). Furthermore, these minerals have been focused on as a functional material owing to their several exceptional physical and chemical properties such as the high fusion temperature, high chemical durability and wide stability fields, etc. (see also reviewed papers: e.g. Boatner 2002, Kolitsch and Holstam 2004, Clavier et al. 2011).

The X-ray analyses for these minerals has been conducted by Ni et al. (1995). Monazite has monoclinic symmetry with space group $P2_1/n$, and preferentially incorporates LREE (light rare earth elements, here La~Gd). On the other hand, xenotime has tetragonal symmetry with space group $I4_1/amd$ (isostructure with zircon), and preferentially incorporates HREE (heavy rare earth elements, here Tb~Lu + Y). Monazite and xenotime can contain trace amount of hydrogen as nominally anhydrous minerals (NAMs). However, only few studies have been reported on infrared spectroscopic measurements of monazite and xenotime. In this study, we conducted polarized infrared spectroscopic observation on hydrothermally synthesized monazite (LaPO₄) and xenotime (YPO₄) single crystals.

The single crystals of monazite and xenotime, synthesized with a piston-cylinder apparatus under a pressure of 1.0 GPa and cut perpendicular and parallel to the elongated direction, are mounted and doubly polished (i.e., monazite: E is nearly perpendicular to Y or Z , xenotime: $E \perp c$ or a). The polarized infrared spectra of monazite and xenotime single crystals were measured in the transmission mode by Nicolet iN10 (Thermo Scientific Inc.).

Monazite crystals show two pleochroic absorption bands at 3164 cm⁻¹ (FWHM = ca. 50 cm⁻¹) and around 3330 cm⁻¹ (FWHM = ca. 140 cm⁻¹). On the other hand, xenotime crystals show a pleochroic absorption band at 3302 cm⁻¹ (FWHM = ca. 10 cm⁻¹). According to obtained absorption figures, the OH dipole in monazite is weakly oriented to [110], while in xenotime, it is strongly oriented perpendicular to c -axis. Based on these results, we suggest the OH incorporation models as shown in Figure 1. Two incorporation models must be considered on monazite due to the n glide symmetric element. The charge balancing mechanism in monazite is expressed as $REE^{3+} \leftrightarrow \square_{REE} + 3H^+$. In contrast, the charge balance in xenotime is maintained by the reaction of $REE^{3+} + O^{2-} \leftrightarrow \square_{REE} + \square_O + H^+$. When the Libowitzky (1999) correlation is applied to the obtained band positions (monazite: 3164 cm⁻¹ and 3330 cm⁻¹, xenotime: 3302 cm⁻¹), the O-O distance of 2.69, 2.76 and 2.74 Å is estimated, respectively. Considering the estimated inter-atomic distance and our OH incorporation models, we could suggest the formation of vacant REE site cause the slight deformation of monazite and xenotime crystal lattices.

Keywords: Monazite, Xenotime, Hydrothermal syntheses, Nominally Anhydrous Minerals, Polarized infrared spectroscopy

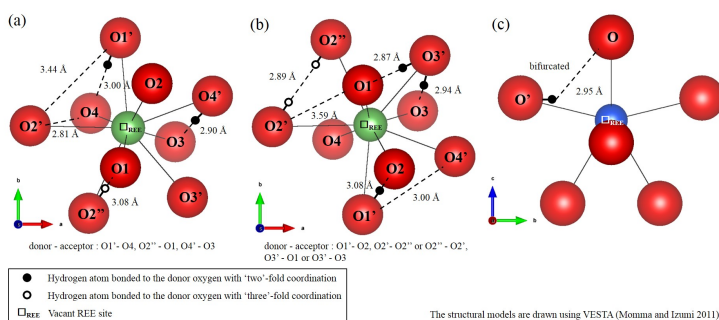


Figure 1. OH incorporation models of monazite (a), (b) and xenotime (c). (a), (b) Two types of hydrogen sites, which corresponding to the coordination number of the donor oxygen, are considered. The two band positions at 3164 cm⁻¹ and 3330 cm⁻¹ would be brought by the coordination number difference of the donor oxygen. (c) The hydrogen position would demand a bifurcated hydrogen bonding. This incorporation model is also proposed by Talla et al. (2011). Additionally in zircon (isostructural with xenotime), the same incorporation model is proposed by Nasdala et al. (2001).

The site and coordination number of oxygen atom in monazite and xenotime can be summarized as below. The oxygen atom in monazite occupies the four general positions (from O1 to O4). O1, O3 and O4 bond with two REE atoms and one P atom. Only O2 bonds with three REE atoms and one P atom. On the other hand, the oxygen atom in xenotime has only one site placed in a mirror plane, and bonds with two REE atoms and one P atom. For more details, see also Ni et al. (1995).